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Fermi and Coulomb correlated relativistic local-density method for atoms

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A parameter-free local-density method called the Ξ method was developed earlier for atoms [N. Vaidehi and M. S. Gopinathan, Phys. Rev. A **29**, 1679 (1984)]. This method, which considered only the Fermi correlation in the potential, was shown to be close to Hartree-Fock accuracy. Its relativistic extension [V. Selvaraj and M. S. Gopinathan, Phys. Rev. A **29**, 3007 (1984)] was also shown to give results that were close to Dirac-Hartree-Fock accuracy. In the present article, the relativistic Ξ method is modified by incorporating the spin-orbit interaction term in the Hamiltonian and the Coulomb correlation between the electrons of opposite spin. Using this fully correlated relativistic method, total energy, expectation values of r^n ($n=-1,1,2$), and spin-orbit parameters for various atoms are calculated. Correlation energies for all the atoms in the Periodic Table are reported. Ionization energy and electron affinity of atoms are also discussed.

I. INTRODUCTION

A parameter-free local-density (LD) method, called the Ξ method,[1] was proposed earlier by Vaidehi and Gopinathan for atomic structure calculations. In the Ξ method, the exchange potential is separated into a self-interaction potential which is evaluated exactly and a pure exchange potential which is treated using a Fermi hole formalism developed[2,3] earlier. The Ξ method was shown[1] to be near Hartree-Fock (HF) accuracy by numerical calculations of the total energy and orbital energies of various atoms. The relativistic extension of the Ξ method, called the RΞ method, has been implemented and shown[4] to be close to Dirac-Hartree-Fock[5-7] (DHF) accuracy.

The most rigorous way of doing the relativistic calculations is the DHF method[6,8] developed by Grant. In the DHF method, the one-electron operator is the Dirac one-electron Hamiltonian and the two-electron operator is the same as in the nonrelativistic Hamiltonian. For each set of quantum numbers n, l, and j there are two radial wave functions, called large and small components, to be solved in the DHF method under the central-field approximation. As in the nonrelativistic case, the DHF nonlocal exchange potential can be approximated by Slater's exchange potential.[9] This method, called the Dirac-Hartree-Fock-Slater (DHFS) method,[10] is somewhat simpler than the DHF method. Xu, Rajagopal, and Ramana[11] have developed a relativistic spin-density-functional theory for the inhomogeneous electron gas. Relativistic effects in atoms and molecules can be calculated from the Schrödinger wave function. This method is called relativistic-Hartree-Fock (RHF) method.[12-16] Cowan and Griffin[17] proposed a method in which the major relativistic effects were included in the calculation within the nonrelativistic model. Following the work of Cowan and Griffin, Selvaraj and Gopinathan[4] proposed a relativistic Ξ method for atomic structure calculations.

The HF (Ref. 18) theory for atoms and theories mentioned above incorporate Fermi correlation between electrons of same spin but do not take into account the Coulomb correlation between electrons of opposite spin. The error due to the neglect of Coulomb correlation becomes serious when one considers small energy differences between electronic states, as in the transition energy and rotational barrier in molecules. The need to go beyond the HF formalism has been recognized for some time, and methods such as configuration interaction (CI),[19] power-series expansion,[20] electron-pair theories,[21] and many-body perturbation theory[22] have been developed to describe Coulomb correlation. However, these methods become conceptually and computationally tedious when applied to systems with a large number of electrons. The local-density method, which expresses the correlation as a function of the one-electron density has been used to describe Coulomb correlation in atoms.[23-33] Such methods employ the uniform electron-gas model for exchange-correlation potential and are often heavily parametrized. The local-spin-density approximation predicts[23,24] correlation energies for atoms that are about twice the exact values. Keller and Gazquez[31] and Manoli and Whitehead[32] derived a Coulomb correlation potential on the basis of a certain shape for the Coulomb hole. Gradient corrections to correlation energy have been proposed by Langreth and co-workers[34-36] and recently by Perdew.[37] Work on the local and nonlocal spin-density-functional calculations of correlation energy has been reviewed by Carroll, Bader, and Voska.[38] It has been established[39,40] that, to describe Coulomb correlation properly, the wave function must satisfy Kato's cusp condition.[41] It is also known[40,42] that the cusp condition is not satisfied by the limited CI wave function. Rajagopal, Kimball, and Banerjee[43] have, along the lines followed by McWeeny,[39] suggested the possibility of modeling the pair correlation function so as to satisfy the cusp condition.

The formalism of the RΞ method is deficient in the following aspects: (i) the spin-orbit interaction is treated as perturbation even though it is of order α^2 (α being the fine-structure constant), and (ii) correlation between electrons of same spin is treated following the Fermi hole formalism[2] but Coulomb hole correlation between electrons of opposite spin is not included. In the present paper, we modify the formalism to overcome both these deficiencies. The spin-orbit interaction is incorporated in the Hamiltonian and thus the modified RΞ method distinguishes the spin-orbit levels for electrons with $l \neq 0$, unlike the RΞ method. The modification of the RΞ method is presented in Sec. II. In Sec. III, we present the derivation of Coulomb hole correlation potential within the LD formalism such that it satisfies explicitly the cusp condition on the density. Further, we choose to treat the Coulomb hole separately from the Fermi hole so that the known properties of the Coulomb hole can be explicitly incorporated into the model and Coulomb correlation effects can be isolated and studied. The separate treatment of the Fermi hole and Coulomb hole is also suggested by Stoll, Golka, and Preuss,[27] and Kemister and Nordholm.[44] In Sec. IV, the final self-consistent-field (SCF) one-electron equations with relativistic and correlation potential obtained by combining the modified RΞ method and the Coulomb correlation potential derived on the basis of the variational theorem are presented. Results of the present method, called the RCΞ method, for total energy, correlation energy, spin-orbit parameter, expectation value of r^n ($n=-1,1,2$), ionization energy, and electron affinity for various atoms are discussed in Sec. V.

II. MODIFIED RΞ METHOD

Before we discuss the modification of the RΞ method, we recall the features of the Ξ method.[1] In the Ξ method, the total energy for the atom or ion can be written as (in rydberg units)

$$\langle E\rangle=\sum_i \int n_i u_i^*(r) f_1 u_i(r)+\tfrac{1}{2}\int \rho(r)\rho(r')g_{rr'}dr\,dr'$$

$$+\tfrac{1}{2}\int \rho_\uparrow(r)V_\uparrow^F(r)dr+\tfrac{1}{2}\int \rho_\downarrow(r)V_\downarrow^F(r)dr \,, \qquad (1)$$

where n_i is the ith orbital occupancy, u_i is the spin orbital, and

$$f_1=-\nabla^2-2Z/r,\quad g_{rr'}=2/|r-r'| \,, \qquad (2)$$

$$\rho_\uparrow(r)=\sum_{i,\uparrow} n_i u_i^*(r)u_i(r) \,, \qquad (3)$$

$$\rho(r)=\rho_\uparrow(r)+\rho_\downarrow(r) \,, \qquad (4)$$

with a similar expression for $\rho_\downarrow(r)$. $V_\uparrow^F(r)$ is the exchange potential at point r for the up-spin electrons, $\rho_\uparrow(r)$ is the total charge density of the up-spin electrons, and $\rho(r)$ is the total charge density. The exchange potential is separated into two parts: (i) a self-interaction part which is evaluated exactly, and (ii) a pure exchange potential which is approximated as using the Fermi hole formalism of Ref. 1, without any adjustable parameter. For the up-spin electron, the exchange potential can be written as

$$V_\uparrow^F(r)=V_\uparrow^{\mathrm{SI}}(r)+V_\uparrow^{\mathrm{ex}}(r) \,. \qquad (5)$$

The expressions for the self-interaction potential at point r, $V_\uparrow^{\mathrm{SI}}(r)$, and pure exchange potential at point r, $V_\uparrow^{\mathrm{ex}}(r)$, for up spin electrons are given as

$$V_\uparrow^{\mathrm{SI}}(r)=-\sum_{i,\uparrow}\frac{(n_i u_i^*(r)u_i(r)\int n_i u_i(r')u_i(r')g_{rr'}dr'}{\rho_\uparrow(r)} \,, \qquad (6)$$

$$V_\uparrow^{\mathrm{ex}}(r)=-4\pi^{1/3}(2^{1/3}-1)\left[\frac{1}{n_\uparrow}+\frac{1}{3}\right]^{-2/3}$$

$$\times\sum_{i,\uparrow}\frac{\rho'_{i,\uparrow}(r)\rho_\uparrow^{-2/3}(r)n_i u_i(r)u_i(r)}{\rho_\uparrow(r)} \,, \qquad (7)$$

with similar expressions for down-spin electrons. In Eq. (7) $\rho'_{i,\uparrow}(r)$ represents the density of electrons of up spin at point r excluding the density of the up-spin electron in the spin-orbital $u_i(r)$

$$[\rho'_{i,\uparrow}(r)]_\uparrow=\sum_{j(\neq i)\uparrow} n_j u_j^*(r)u_j(r) \,. \qquad (8)$$

By variational minimization of the total energy of Eq. (1) with respect to spin orbitals $\{u_i\}$ subject to their normalization, we get a set of one-electron Schrödinger equations

$$[f_1+v^C(r)+v_\uparrow^{\mathrm{Si}}(r)+v_\uparrow^{\mathrm{ex}}(r)][u_i(r)]_\uparrow=\varepsilon_i[u_i(r)]_\uparrow \,, \qquad (9)$$

where $v^C(r)$, the Coulombic electron-electron repulsion potential, is

$$v^C(r)=\sum_j n_j\int u_j^*(r')u_j(r')\frac{2}{|r-r'|}dr' \,, \qquad (10)$$

$v_\uparrow^{\mathrm{SI}}(r)$, the self-interaction potential, is

$$v_\uparrow^{\mathrm{SI}}(r)=-n_i\int u_i^*(r')u_i(r')\frac{2}{|r-r'|}dr' \,, \qquad (11)$$

and $v_\uparrow^{\mathrm{ex}}(r)$, the one-electron pure exchange potential in the Ξ method, is

$$v_\uparrow^{\mathrm{ex}}(r)=-4\pi^{1/3}(2^{1/3}-1)\left[\frac{1}{n_\uparrow}+\frac{1}{3}\right]^{-2/3}\left[2\rho_i(r)\rho_\uparrow^{-2/3}(r)-\tfrac{2}{3}\rho_\uparrow^{-5/3}(r)\sum_{i,\uparrow} n_i u_i^*(r)u_i(r)\rho'_{i,\uparrow}(r)\right] \,. \qquad (12)$$

Note that we denote the average potential in the total-energy expression, Eq. (1), by V and the corresponding variationally obtained potential of the one-electron equation, Eq. (9), by v.

We now discuss the modification of the RΞ method. In the RΞ method, the major relativistic corrections, namely, mass-velocity correction and Darwin correction are included in the Hamiltonian, but the j-dependent spin-orbit interaction term, which is also of order of α^2 (fine-structure constant), was not included. We have presently modified the RΞ method by incorporating the spin-orbit interaction term in the Hamiltonian. The one-electron SCF equation used in the RΞ method is

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+v(r)+H_m(r)+H_D(r)\right]P_{nl}(r)=\varepsilon_{nl}P_{nl}(r)\ , \tag{13}$$

where $v(r)$, the central field potential, is

$$v(r)=-2Z/r+v^C(r)+v_\uparrow^{\mathrm{SI}}(r)+v_\uparrow^{\mathrm{ex}}(r)\ , \tag{14}$$

$H_m(r)$, the mass-velocity correction, is

$$H_m(r)=K[\varepsilon_{nl}-v(r)]^2\ , \tag{15}$$

and $H_D(r)$, the Darwin correction, is

$$H_D(r)=KB\frac{dv(r)}{dr}\left[\frac{d}{dr}-\frac{1}{r}\right]\ , \tag{16}$$

with

$$K=-\frac{\alpha^2}{4},\quad B=\left[1+\frac{\alpha^2}{4}[\varepsilon_{nl}-v(r)]\right]^{-1}\ . \tag{17}$$

Equation (13) is now modified by incorporating the spin-orbit interaction term in the Hamiltonian, and thus the one-electron equation of the modified RΞ method becomes

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+v(r)+H_m(r)+H_D(r)+H_{\mathrm{s.o.}}(r)\right]P_{nlj}(r)=\varepsilon_{nlj}P_{nlj}(r)\ , \tag{18}$$

where $H_{\mathrm{s.o.}}(r)$, the spin-orbit interaction term, is

$$H_{\mathrm{s.o.}}(r)=KB\Lambda\frac{dv(r)}{dr}\frac{1}{r}\ , \tag{19}$$

where Λ is equal to $l+1$ for $j=l+\frac{1}{2}$ and it is $-l$ for $j=l-\frac{1}{2}$. The approximate one-electron Hamiltonian, given by Eq. (19), commutes with the operators J^2, L^2, and S^2. The present method distinguishes between the spin-orbit levels for electrons with $l\neq 0$, making the wave functions $P_{nlj}(r)$ dependent on the quantum number j.

III. FORMULATION OF THE COULOMB-HOLE POTENTIAL

We start with the total-energy expression, Eq. (1), of the Ξ method. With Coulomb correlation, the total energy can be written as

$$\begin{aligned}\langle E\rangle=\sum_i\int n_iu_i^*(r)f_1u_i(r)+\tfrac{1}{2}\int\rho(r)\rho(r')g_{rr'}dr\,dr'\\+\tfrac{1}{2}\int\rho_\uparrow(r)V_\uparrow^F(r)dr+\tfrac{1}{2}\int\rho_\downarrow(r)V_\downarrow^F(r)dr\\+\tfrac{1}{2}\int\rho_\uparrow(r)V_\uparrow^{\mathrm{corr}}(r)dr+\tfrac{1}{2}\int\rho_\downarrow(r)V_\downarrow^{\mathrm{corr}}(r)dr\ ,\end{aligned} \tag{20}$$

where $V_\uparrow^{\mathrm{corr}}(r)$ is the Coulomb correlation potential acting upon an up-spin electron, the potential being produced by all the down-spin electrons. Thus we have expressed the Coulomb correlation energy of the atom as

$$E^{\mathrm{corr}}=\tfrac{1}{2}\int\rho_\uparrow(r)V_\uparrow^{\mathrm{corr}}(r)dr+\tfrac{1}{2}\int\rho_\downarrow(r)V_\downarrow^{\mathrm{corr}}(r)dr\ . \tag{21}$$

Variational minimization of the total energy of Eq. (20) with respect to the spin orbitals $\{u_i\}$ leads to the one-electron equations similar to Eq. (9),

$$[f_1+v^C(r)+v_\uparrow^{\mathrm{SI}}(r)+v_\uparrow^{\mathrm{ex}}(r)+v_\uparrow^{\mathrm{corr}}(r)][u_i(r)]_\uparrow=\varepsilon_i[u_i(r)]_\uparrow\ . \tag{22}$$

In Eq. (22), $v_\uparrow^{\mathrm{corr}}(r)$, the Coulomb correlation potential, remains to be specified. Again note that we denote $V_\uparrow^{\mathrm{corr}}(r)$ as the correlation potential for an up-spin electron and $v_\uparrow^{\mathrm{corr}}(r)$ as the corresponding correlation potential in the variationally derived one-electron equation. In this section we proceed to derive an analytical expression for $v_\uparrow^{\mathrm{corr}}(r)$.

The Coulomb correlation potential for an up-spin electron can be thought of as arising due to the removal of charge of down-spin electrons from its vicinity. This depletion of charge is usually called the Coulomb hole. Knowledge of the shape and size of the Coulomb hole enables one to derive the Coulomb correlation potential $v_\uparrow^{\mathrm{corr}}(r)$.

Two important properties of the Coulomb hole which are of relevance to the present work are the following.

(i) The Coulomb-hole density should satisfy Kato's cusp condition.[45]

(ii) The total Coulomb charge is zero, i.e., the Coulomb-hole density integrates to zero over the entire range of the Coulomb hole.[39]

Using these two properties we now proceed to derive an expression for the Coulomb-hole density, $\rho^{Ch}(r)$.

The differential form of Kato's cusp condition on the wave function is equivalent to the integral form[45]

$$\Psi(r_1,r_2,r_3,\ldots,r_n)=\Psi(r_1,r_1,r_3,\ldots,r_n)(1+\tfrac{1}{2}r_{12}) \tag{23}$$

for small r_{12}, where $r_{12}=|r_1-r_2|$. Squaring both sides of Eq. (23) and neglecting higher powers of r_{12}, we get, for small r_{12},

$$\Psi^2(r_1,r_2,r_3,\ldots,r_n)=\Psi^2(r_1,r_1,r_3,\ldots,r_n)(1+r_{12})\ . \tag{24}$$

Integrating both sides of Eq. (24) over the coordinates of all the electrons except electrons 1 and 2, we have

$$\Pi(r_1,r_2)=\Pi(r_1,r_1)(1+r_{12})\ , \tag{25}$$

where $\Pi(r_1,r_2)$, the pair density function, is defined as

$$\Pi(r_1,r_2)=n(n-1)\int \Psi^2(r_1,r_2,r_3,\ldots,r_n)d\tau_3 d\tau_4\cdots d\tau_n \ . \tag{26}$$

The pair density can be generally broken down into its spin components as

$$\Pi(r_1,r_2)=\Pi_{\uparrow\downarrow}(r_1,r_2)+\Pi_{\downarrow\uparrow}(r_1,r_2)+\Pi_{\uparrow\uparrow}(r_1,r_2)+\Pi_{\downarrow\downarrow}(r_1,r_2) \ . \tag{27}$$

Hence we set, using Eqs. (25) and (27),

$$\Pi_{\uparrow\downarrow}(r_1,r_2)=\Pi_{\uparrow\downarrow}(r_1,r_1)(1+r_{12}) \tag{28}$$

with similar equations for the other spin components of $\Pi(r_1,r_2)$.

Here we shall neglect Coulomb correlation between electrons of like spin and consider the Coulomb correlation between electrons of unlike spins only. This is reasonable because Fermi correlation for electrons of like spin keeps them apart in space and hence Coulomb correlation between such electrons may be neglected to a good approximation.

The pair density calculated using the correlated wave function in Eq. (26) may be called the correlated pair density and we denote it as $\Pi^{\text{corr}}(r_1,r_2)$ and that calculated using the uncorrelated wave function may be called independent pair density denoted as $\Pi^{\text{ind}}(r_1,r_2)$. The relation between the two can be formally written in terms of a correlation function $f_{\uparrow\downarrow}(r_1,r_2)$ as

$$\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r_2)=\Pi^{\text{ind}}_{\uparrow\downarrow}(r_1,r_2)[1+f_{\uparrow\downarrow}(r_1,r_2)] \ , \tag{29}$$

with similar expressions for other spin components. The expression for the correlation function $f_{\uparrow\uparrow}(r_1,r_2)$ has been derived earlier[1] in the treatment of the Fermi correlation by the Ξ method. Here we are interested in the derivation of an explicit form for $f_{\uparrow\downarrow}(r_1,r_2)$.

The independent pair density can be written as the product of one-electron densities as

$$\Pi^{\text{ind}}_{\uparrow\downarrow}(r_1,r_2)=\rho_{\uparrow}(r_1)\rho_{\downarrow}(r_2) \ . \tag{30}$$

For later convenience we fix the reference electron at r_1 and take this to be the origin for interelectronic distances. The distance measured from r_1 is denoted as r'. In this notation Eq. (29) is

$$\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r')=\rho_{\uparrow}(r_1)\rho_{\downarrow}(r')[1+f_{\uparrow\downarrow}(r_1,r')] \ , \tag{31}$$

where Eq. (30) has been used. Thus the conditional probability of finding a down-spin electron at r' when an electron of up spin is known to be at r_1 can be written as

$$\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r')/\rho_{\uparrow}(r_1)=\rho_{\downarrow}(r')+\rho_{\downarrow}(r')f_{\uparrow\downarrow}(r_1,r') \ . \tag{32}$$

The second term on the right-hand side of this equation represents the amount by which the independent electron density at r', viz., $\rho_{\downarrow}(r')$ is affected by Coulomb correlation. Therefore this term corresponds to the Coulomb-hole density at r' which we denote as $\rho^{Ch}_{\uparrow}(r')$ since it is produced by an up-spin electron at r_1. Thus

$$\rho^{Ch}_{\uparrow}(r')=\rho_{\downarrow}(r')f_{\uparrow\downarrow}(r_1,r') \ . \tag{33}$$

For small values of r', the Coulomb-hole density is negative, which implies a negative $f_{\uparrow\downarrow}$. However, the Coulomb-hole density becomes positive at large r' in order to satisfy property (ii) of the Coulomb hole mentioned above, namely, that the total Coulomb-hole charge is zero. This means that $f_{\uparrow\downarrow}(r_1,r')$ becomes positive at large r'. A schematic sketch of the Coulomb hole is shown in Fig. 1.

A functional form for $f_{\uparrow\downarrow}(r_1,r')$ can be derived as follows. Equation (31), which we derived on the basis of the cusp condition, can be rewritten by dividing both sides by $\rho_{\uparrow}(r_1)$ and changing over to the present notation as

$$\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r')/\rho_{\uparrow}(r_1)=\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r_1)(1+r')/\rho_{\uparrow}(r_1) \ . \tag{34}$$

Comparing Eqs. (32) and (34) we have

$$\rho_{\downarrow}(r')[1+f_{\uparrow\downarrow}(r_1,r')]=\Pi^{\text{corr}}_{\uparrow\downarrow}(r_1,r_1)(1+r')/\rho_{\uparrow}(r_1) \ . \tag{35}$$

The point $(r_C)_{\uparrow}$ in Fig. 1 at which the Coulomb-hole density changes sign may be called the Coulomb-hole radius, beyond which $\rho^{Ch}(r')$ is positive. At $(r_C)_{\uparrow}$ we have

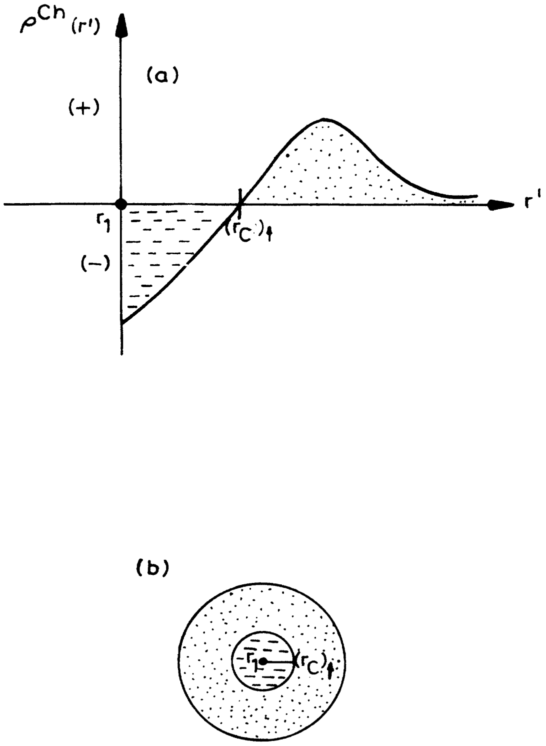

FIG. 1. (a) Variation of Coulomb-hole density $\rho^{Ch}(r')$ as a function of the distance r' from the reference electron at r_1. (b) A view of the spherical Coulomb hole in the present model. $(r_C)_{\uparrow}$ is the radius of the Coulomb hole.

$$\rho_{\uparrow}^{Ch}((r_C)_{\uparrow})=\rho_{\downarrow}((r_C)_{\uparrow})f_{\uparrow\downarrow}(r_1,(r_C)_{\uparrow})=0\ . \tag{36}$$

Hence for $r'=(r_C)_{\uparrow}$, Eq. (35) can be rewritten as

$$\Pi_{\uparrow\downarrow}^{\text{corr}}(r_1,r_1)=\rho_{\uparrow}(r_1)\rho_{\downarrow}((r_C)_{\uparrow})[1+(r_C)_{\uparrow}]^{-1}\ . \tag{37}$$

Substituting Eq. (37) into Eq. (35) we get

$$\begin{aligned}\rho_{\downarrow}(r')f_{\uparrow\downarrow}(r_1,r')\\ &=\rho_{\downarrow}((r_C)_{\uparrow})(1+r')[1+(r_C)_{\uparrow}]^{-1}-\rho_{\downarrow}(r')\ .\end{aligned} \tag{38}$$

The left-hand side of Eq. (38) corresponds to the Coulomb-hole density as defined by Eq. (33) and hence

$$\rho_{\uparrow}^{Ch}(r')=\rho_{\downarrow}((r_C)_{\uparrow})(1+r')[1+(r_C)_{\uparrow}]^{-1}-\rho_{\downarrow}(r')\ . \tag{39}$$

For small values of r' we now assume that the independent one-electron density $\rho_{\uparrow}(r_1)$ varies slowly so that we may set

$$\rho_{\downarrow}((r_C)_{\uparrow})=\rho_{\downarrow}(r')=\rho_{\downarrow}(r_1)\ , \tag{40}$$

and Eq. (39) becomes

$$\rho_{\uparrow}^{Ch}(r')=\rho_{\downarrow}(r_1)[r'-(r_C)_{\uparrow}][1+(r_C)_{\uparrow}]^{-1}\ . \tag{41}$$

This equation gives the Coulomb-hole density $\rho_{\uparrow}^{Ch}(r')$ for small values of r'. Notice that we have derived this from the cusp condition for the exact wave function, imposing the assumption of a slowly varying density as given by Eq. (40). This is obviously not valid at large r' and the Coulomb-hole density $\rho_{\uparrow}^{Ch}(r')$ of Eq. (41) varies linearly with r' instead of vanishing at large r', as it should (see Fig. 1). In order to correct for this wrong behavior at large r', we introduce in an *ad hoc* manner the factor $\exp(-cr')$ in Eq. (41):

$$\rho_{\uparrow}^{Ch}(r')=\rho_{\downarrow}(r_1)[r'-(r_C)_{\uparrow}][1+(r_C)_{\uparrow}]^{-1}\exp(-cr')\ . \tag{42}$$

The constant c can be determined from property (ii) of the Coulomb hole. With the additional assumption that the Coulomb hole is spherically symmetric,[29] the property (ii) that the Coulomb-hole charge is zero becomes

$$\begin{aligned}4\pi\int_0^{\infty}\rho_{\uparrow}^{Ch}(r')r'^2dr'\\ &=4\pi\int_0^{\infty}\rho_{\downarrow}(r_1)[r'-(r_C)_{\uparrow}][1+(r_C)_{\uparrow}]^{-1}\\ &\quad\times\exp(-cr')r'^2dr'=0\ ,\end{aligned} \tag{43}$$

where we have used Eq. (42). Carrying out the integration in Eq. (43) gives

$$c=3/(r_C)_{\uparrow}\ , \tag{44}$$

so that Eq. (42) yields

$$\begin{aligned}\rho_{\uparrow}^{Ch}(r')&=\rho_{\downarrow}(r_1)[r'-(r_C)_{\uparrow}][1+(r_C)_{\uparrow}]^{-1}\\ &\quad\times\exp[-3r'/(r_C)_{\uparrow}]\ .\end{aligned} \tag{45}$$

Using this expression for the Coulomb-hole density for an up-spin electron, we now proceed to derive the corresponding Coulomb correlation potential. For the spherical Coulomb hole, the potential at the center of the hole, r_1, is

$$\begin{aligned}V_{\uparrow}^{\text{corr}}(r_1)&=4\pi\int_0^{\infty}\rho_{\uparrow}^{Ch}(r')r'dr'\\ &=4\pi\int_0^{\infty}\rho_{\downarrow}(r_1)[r'-(r_C)_{\uparrow}][1+(r_C)_{\uparrow}]^{-1}\\ &\quad\times\exp[-3r'/(r_C)_{\uparrow}]r'dr'\ ,\end{aligned} \tag{46}$$

which on integration gives (in rydberg units)

$$V_{\uparrow}^{\text{corr}}(r_1)=-(8\pi/27)(r_C)_{\uparrow}^3[1+(r_C)_{\uparrow}]^{-1}\rho_{\downarrow}(r_1)\ . \tag{47}$$

Now the following comments may be made. The Coulomb correlation potential of Eq. (47) is negative, as it should be. Further, in the present LD formalism, $V_{\uparrow}^{\text{corr}}(r_1)$ is the same for all spin orbitals of the same spin ($\uparrow$), as it depends only on $\rho_{\uparrow}(r_1)$ and $(r_C)_{\uparrow}$ and not specifically on $[u_i(r_1)]_{\uparrow}$.

In order to completely specify $V_{\uparrow}^{\text{corr}}(r_1)$, we must determine $(r_C)_{\uparrow}$, the radius of the Coulomb hole. We notice from Eq. (45) that the Coulomb-hole density for an up-spin electron depends on the down-spin density at the center of the hole. Therefore it is reasonable to expect the radius of the Coulomb hole for an up-spin electron to depend on the down-spin density. The relation between the radius and density has been derived earlier for the Fermi hole as[2]

$$(r_F)_{\downarrow}=\left[\pi\left[\frac{1}{n_{\downarrow}}+\frac{1}{3}\right]\rho_{\downarrow}(r_1)\right]^{-1/3}\ . \tag{48}$$

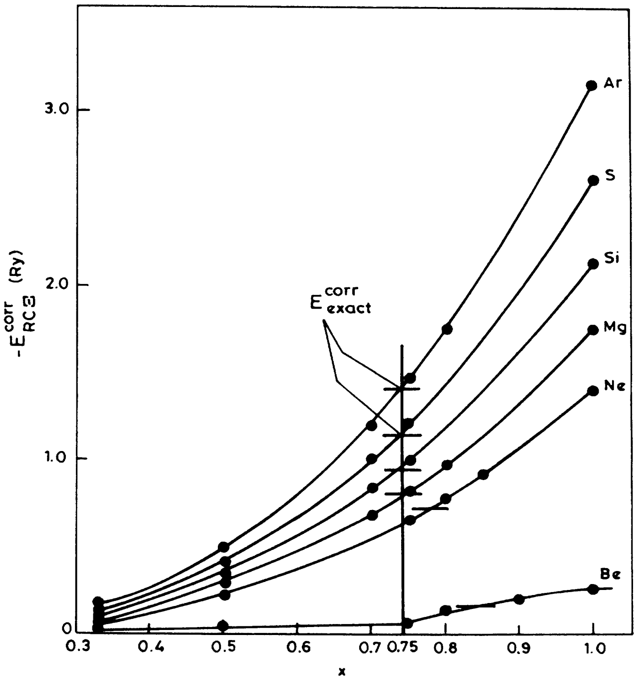

FIG. 2. Parametrization of the ratio x between Coulomb-hole and Fermi-hole radii. ● denotes the correlation energy calculated by the present method for various x values for different atoms. The horizontal line denotes the exact value of the correlation energy calculated using Eq. (52) of text.

We now assume the same functional dependence for the radius of the Coulomb hole and set

$$(r_C)_\uparrow = x(r_F)_\downarrow = x\left[\pi\left[\frac{1}{n_\downarrow}+\frac{1}{3}\right]\rho_\downarrow(r_1)\right]^{-1/3} , \tag{49}$$

where x, the ratio between the Coulomb- and Fermi-hole radii, is introduced as a parameter. The determination of x will be discussed later.

Substituting Eq. (49) in Eq. (47), we have

$$\begin{aligned} V_\uparrow^{\mathrm{corr}}(r_1) = -8/27x^3 &\left[\pi\left[\frac{1}{n_\downarrow}+\frac{1}{3}\right]\rho_\downarrow(r_1)\right]^{-1} \\ &\times \Bigg\{ x\left[\pi\left[\frac{1}{n_\downarrow}+\frac{1}{3}\right]\rho_\downarrow(r_1)\right]^{-1/3} \\ &+1 \Bigg\}^{-1} \rho_\downarrow(r_1) , \end{aligned} \tag{50}$$

We can use this expression for $V_\uparrow^{\mathrm{corr}}(r_1)$ in Eq. (20) for total energy, together with a similar expression for $V_\downarrow^{\mathrm{corr}}(r_1)$. The resulting expression for $\langle E \rangle$ is then variationally minimized with respect to the spin orbitals $\{u_i\}$ as described earlier. This gives the set of one-electron equations of the form of Eq. (22) wherein the variationally correct Coulomb correlation potential is now given by

$$\begin{aligned} v_\uparrow^{\mathrm{corr}}(r_1) = -\frac{4\pi}{27}\rho_\downarrow(r_1) &\left[\frac{(r_C^3)_\uparrow}{1+(r_C)_\uparrow}+\frac{(r_C^3)_\downarrow}{1+(r_C)_\downarrow}\right] \\ &+\frac{4x}{81}\pi^{2/3}\left[\frac{1}{n_\uparrow}+\frac{1}{3}\right]^{-1/3}\rho_\uparrow^{-1/3}(r_1)\rho_\downarrow(r_1) \\ &\times\left[\frac{[3(r_C^2)_\downarrow+2(r_C^3)_\downarrow]}{[1+(r_C)_\downarrow]^2}\right] , \end{aligned} \tag{51}$$

with a similar expression for $v_\downarrow^{\mathrm{corr}}(r_1)$. Here $(r_C)_\uparrow$ is given by Eq. (49). The terms in Eq. (51) arise from the differentiation of the fifth and the sixth terms of the total-energy expression, Eq. (20) after the substitution for $V_\uparrow^{\mathrm{corr}}(r_1)$ from Eq. (50). Though the expression, Eq. (51), looks involved, it is simply a local-density expression and is immediately computed once the densities $\rho_\uparrow(r)$ and $\rho_\downarrow(r)$ are given.

The specification of the potential terms in the one-electron equations [Eq. (22)] is now complete through Eqs. (10)–(12) and (51), along with Eq. (49), except for the parameter x. The solutions of Eq. (22) are "fully correlated orbitals" in the sense that Fermi and Coulomb correlations are now included explicitly and they are exactly self-interaction corrected.

We now determine the parameter x occurring in Eq. (49), which represents the ratio of the Coulomb- and Fermi-hole radii by comparing the correlation energy calculated by the present method using the Eq. (21) with the "exact" correlation energy which is obtained by the following equation:

$$E_{\mathrm{exact}}^{\mathrm{corr}} = E^{\mathrm{expt}} - E^{\mathrm{DHF}} - \Delta E^{\mathrm{Lamb}} . \tag{52}$$

Here E^{expt} is the experimental total energy,[46] E^{DHF} the fully relativistic DHF total energy,[6] and ΔE^{Lamb} the Lamb correction to the total energy.[47] The value of x has been presently determined for atoms Be, B, Mg, Si, P, and Ar. Figure 2 shows a plot of the correlation energy calculated by the present method versus x for these atoms. The optimum value of x for which the calculated value of correlation energy is equal to the exact correlation energy of Eq. (52), is seen to be 0.85 for Be, but quickly attains a value close to 0.75 for heavier atoms. $E_{\mathrm{exact}}^{\mathrm{corr}}$ values for atoms with $Z > 18$ do not seem to be available in the literature. In view of the above trend we have chosen to use a universal value of 0.75 for all atoms.

IV. FULLY CORRELATED RELATIVISTIC (RCΞ) METHOD

In Sec. II we developed a method to incorporate all major relativistic corrections in the Ξ method and in Sec. III we derived the Coulomb correlation potential to treat the Coulomb hole. The fully correlated relativistic Ξ method is obtained by combining these two methods. The final one-electron SCF equation of the present spin-polarized method can be given as

$$\begin{aligned} \Bigg[\Bigg\{ -\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-\frac{2Z}{r}+v^C(r)+v_\uparrow^{\mathrm{SI}}(r)+v_{i,\uparrow}^{\mathrm{ex}}(r)+v_\uparrow^{\mathrm{corr}}(r) \Bigg\} &-\frac{\alpha^2}{4}[\varepsilon_{nlj}-v(r)]^2 \\ -\frac{\alpha^2}{4}\left\{1+\frac{\alpha^2}{4}[\varepsilon_{nlj}-v(r)]\right\}^{-1}\frac{dv(r)}{dr}\left\{\frac{dP_{nlj}(r)/dr}{P_{nlj}(r)}-\frac{1}{r}\right\}& \\ -\frac{\alpha^2}{4}\left\{1+\frac{\alpha^2}{4}[\varepsilon_{nlj}-v(r)]\right\}^{-1}\Lambda\frac{dv(r)}{dr}\frac{1}{r}\Bigg] P_{nlj}(r) = \varepsilon_{nlj}P_{nlj}(r) ,& \end{aligned} \tag{53}$$

where, $v_\uparrow^{\mathrm{corr}}(r)$, the correlation potential, is given in Eq. (51) and $v(r)$, the central-field potential for the ith orbital, is

$$v(r) = -2Z/r + v^C(r) + v_\uparrow^{\mathrm{SI}}(r) + [v_i^{\mathrm{ex}}(r)]_\uparrow + v_\uparrow^{\mathrm{corr}}(r) . \tag{54}$$

The set of fully correlated and relativistic one-electron equations, Eq. (53), can be solved numerically for atoms and ions using a modified Hermann-Skillman[48] computer program which performs spin-polarized calculations.[3,4] Computationally, the present method is simple and rapid. All the results reported here were computed on a tabletop

PC AT 386 system, on which a heavy-atom such as uranium, for instance, takes about 40 min for a complete SCF calculation.

The orbitals $\{u_i\}$ obtained by this method are not all orthogonal since the orthogonality constraints on the spin orbitals have not been included in the variational minimization procedure in order to keep the formalism simple. This defect of nonorthogonality of the orbitals is known[49] to be small for total energy and orbital energies. However, since we are concerned with quantities of a much smaller magnitude, like correlation energy, it is considered necessary to orthogonalize the orbitals. This is done using Lowdin's orthogonalization procedure[50] at each iteration of the SCF cycle.

V. RESULTS AND DISCUSSIONS

A. Total energy

The average total energy for light, medium, and heavy atoms calculated by the present RCΞ method is given in Table I, along with DHF results.[7] $E^{\rm corr}_{\rm RC\Xi}$ (column 2) represents the correlation energy calculated using Eq. (21), $E^{\rm tot}_{\rm RC\Xi}$ (column 3) represents the total energy calculated using the present method, and column 4, which gives the total energy without the correlation energy, is obtained by subtracting correlation energy (column 2) from total energy (column 3) for the particular atom. The absolute percentage of deviation of the average total energy by the present method (without correlation) from the average total energy of the DHF method is given in column 5. It is seen that the deviation for light and medium atoms is small and the deviation increases for heavy atoms. This may be due to the neglect of the finite-nuclear-size correction which is important for heavy atoms and the neglect of the small-component wave function.

The relativistic correction $\Delta E^{\rm rel}_{\rm RC\Xi}$ to the total energy for various atoms is calculated by using Eq. (55):

$$\Delta E^{\rm rel}_{\rm RC\Xi} = E^{\rm tot}_{\rm RC\Xi} - E^{\rm tot}_{\Xi} - E^{\rm corr}_{\rm RC\Xi} \,, \tag{55}$$

where $E^{\rm tot}_{\rm RC\Xi}$ and $E^{\rm corr}_{\rm RC\Xi}$ are defined earlier, and $E^{\rm tot}_{\Xi}$ represents the total energy by the Ξ method.[1] The relativistic correction by the DHF method[7] is calculated as the difference between the average DHF total energy and the nonrelativistic HF average total energy[51,52] for the particular atom. The percentage of relativistic correction

TABLE I. Total energy (Ry).

Atom	$-E^{\rm corr}_{\rm RC\Xi}$ [a]	$-E^{\rm tot}_{\rm RC\Xi}$ [b]	$-E^{\rm tot}_{\rm RC\Xi}$ [c] $-E^{\rm corr}_{\rm RC\Xi}$	Deviation of column 4 from DHF (%)	$-E^{\rm tot}_{\rm DHF}$ [d]
$_{4}$Be	0.1284	29.288	29.161	0.031	29.152
$_{8}$O	0.4269	150.035	149.607	0.029	149.650
$_{10}$Ne	0.6686	258.010	257.342	0.016	257.383
$_{12}$Mg	0.8391	400.668	399.829	0.010	399.869
$_{14}$Si	1.0294	579.881	578.852	0.012	578.924
$_{18}$Ar	1.4862	1058.808	1057.321	0.004	1057.367
$_{22}$Ti	1.9164	1707.444	1705.527	0.007	1705.639
$_{26}$Fe	2.4693	2544.929	2542.459	0.013	2542.786
$_{30}$Zn	3.0787	3592.031	3588.953	0.008	3589.236
$_{36}$Kr	3.8582	5581.349	5577.491	0.004	5577.716
$_{42}$Mo	4.6202	8098.618	8093.998	0.004	8094.287
$_{48}$Cd	5.5171	11 192.369	11 186.851	0.002	11 186.652
$_{50}$Sn	5.7731	12 358.389	12 352.616	0.003	12 353.274
$_{54}$Xe	6.3152	14 900.619	14 894.204	0.003	14 893.801
$_{60}$Nd	7.1674	19 258.763	19 251.596	0.007	19 250.273
$_{64}$Gd	7.8013	22 558.926	22 551.125	0.012	22 548.394
$_{70}$Yb	8.8462	28 149.843	28 140.996	0.019	28 135.439
$_{74}$W	9.4443	32 328.899	32 319.455	0.022	32 312.259
$_{78}$Pt	10.0655	36 890.464	36 880.398	0.029	36 869.734
$_{80}$Hg	10.3929	39 320.583	39 310.189	0.032	39 297.706
$_{82}$Pb	10.6674	41 855.211	41 844.543	0.041	41 827.389
$_{86}$Rn	11.2276	47 239.431	47 228.203	0.041	47 203.956
$_{88}$Ra	11.4638	50 097.361	50 085.897	0.059	50 056.074
$_{92}$U	12.0541	56 161.593	56 149.539	0.079	56 105.041

[a] Correlation energy by the present method.

[b] Total energy by the present method as the sum of correlation energy and the total energy of RCΞ wave function with HF Hamiltonian.

[c] Total energy without correlation (difference between columns 3 and 2) by the present method.

[d] Dirac-Hartree-Fock values taken from Ref. 7.

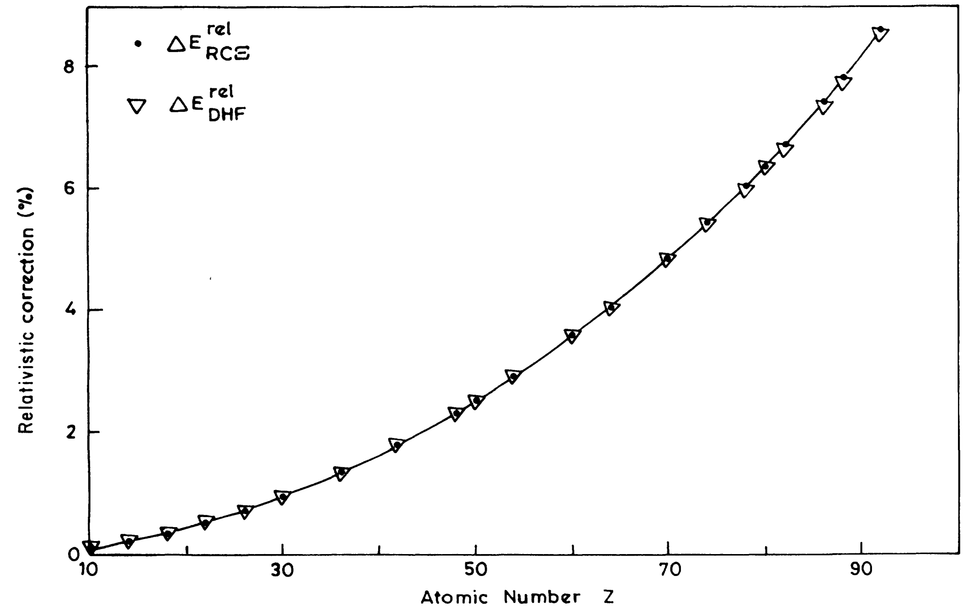

FIG. 3. Percentage of relativistic correction to total energy by RCΞ (present) and DHF methods.

to the total energy by the present RCΞ and the DHF methods is given in Fig. 3. It is evident from Fig. 3 that the relativistic effects are well described by the present method. However, the present method overestimates it by about 0.03% for heavy atoms. This may again be due to the neglect of the small-component wave function and the finite-nuclear-size correction.

B. Correlation energy

As mentioned in Sec. II, the present RCΞ method incorporates the Coulomb correlation explicitly. In order to judge how well this method describes correlation, the most direct method is to calculate the correlation energy and compare it with the "exact" correlation energy,

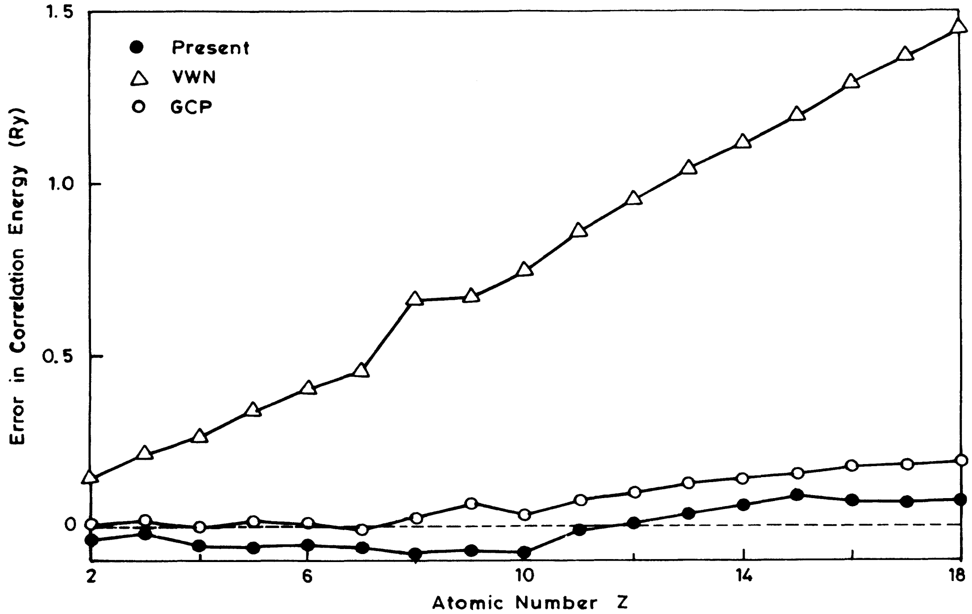

FIG. 4. Error in the correlation energy (Ry) for atoms He to Ar by RCΞ (this work), VWN (Voska, Wilkand, and Nusair, Refs. 30 and 38), and GCP (gradient correction due to Perdew, Refs. 37 and 38) methods.

TABLE II. Coulomb correlation energy (Ry) using the method presented in this paper.

Atom	Relativistic electronic configuration[a]	$-E^{\mathrm{corr}}_{\mathrm{RC\Xi}}$ [b]
$_{2}$He	$1s^{2}_{+}$	0.0443
		0.0840
$_{3}$Li	[He]$2s^{1}_{+}$	0.0703
		0.0892
$_{4}$Be	[He]$2s^{2}_{+}$	0.1284
		0.1860
$_{5}$B	[He]$2s^{2}_{+}\,2p^{1}_{-}$	0.1843
		0.2444
$_{6}$C	[He]$2s^{2}_{+}\,2p^{2}_{-}$	0.2644
		0.3182
$_{7}$N	[He]$2s^{2}_{+}\,2p^{2}_{-}\,2p^{1}_{+}$	0.3455
		0.4072
$_{8}$O	[He]$2s^{2}_{+}\,2p^{2}_{-}\,2p^{2}_{+}$	0.4269
		0.5090
$_{9}$F	[He]$2s^{2}_{+}\,2p^{2}_{-}\,2p^{3}_{+}$	0.5492
		0.6192
$_{10}$Ne	[He]$2s^{2}_{+}\,2p^{2}_{-}\,2p^{4}_{+}$	0.6686
		0.7468
$_{11}$Na	[Ne]$3s^{1}_{+}$	0.7389
		0.7522
$_{12}$Mg	[Ne]$3s^{2}_{+}$	0.8391
		0.8324
$_{13}$Al	[Ne]$3s^{2}_{+}\,3p^{1}_{-}$	0.9264
		0.8910
$_{14}$Si	[Ne]$3s^{2}_{+}\,3p^{2}_{-}$	1.0294
		0.9676
$_{15}$P	[Ne]$3s^{2}_{+}\,3p^{2}_{-}\,3p^{1}_{+}$	1.1314
		1.0428
$_{16}$S	[Ne]$3s^{2}_{+}\,3p^{2}_{-}\,3p^{2}_{+}$	1.2331
		1.1624
$_{17}$Cl	[Ne]$3s^{2}_{+}\,3p^{2}_{-}\,3p^{3}_{+}$	1.3606
		1.2924
$_{18}$Ar	[Ne]$3s^{2}_{+}\,3p^{2}_{-}\,3p^{4}_{+}$	1.4862
		1.4156
$_{19}$K	[Ar]$4s^{1}_{+}$	1.5687
$_{20}$Ca	[Ar]$4s^{2}_{+}$	1.6745
$_{21}$Sc	[Ar]$3d^{1}_{-}\,4s^{2}_{+}$	1.7787
$_{22}$Ti	[Ar]$3d^{2}_{-}\,4s^{2}_{+}$	1.9164
$_{23}$V	[Ar]$3d^{3}_{-}\,4s^{2}_{+}$	2.0720
$_{24}$Cr	[Ar]$3d^{4}_{-}\,3d^{1}_{+}\,4s^{1}_{+}$	2.1793
$_{25}$Mn	[Ar]$3d^{4}_{-}\,3d^{1}_{+}\,4s^{2}_{+}$	2.3346
$_{26}$Fe	[Ar]$3d^{4}_{-}\,3d^{2}_{+}\,4s^{2}_{+}$	2.4693
$_{27}$Co	[Ar]$3d^{4}_{-}\,3d^{3}_{+}\,4s^{2}_{+}$	2.6082
$_{28}$Ni	[Ar]$3d^{4}_{-}\,3d^{4}_{+}\,4s^{2}_{+}$	2.7667
$_{29}$Cu	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{1}_{+}$	2.9420
$_{30}$Zn	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}$	3.0781
$_{31}$Ga	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{1}_{-}$	3.1958
$_{32}$Ge	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{2}_{-}$	3.3253
$_{33}$As	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{2}_{-}\,4p^{1}_{+}$	3.4510
$_{34}$Se	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{2}_{-}\,4p^{2}_{+}$	3.5751
$_{35}$Br	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{2}_{-}\,4p^{3}_{+}$	3.7180
$_{36}$Kr	[Ar]$3d^{4}_{-}\,3d^{6}_{+}\,4s^{2}_{+}\,4p^{2}_{-}\,4p^{4}_{+}$	3.8582
		3.8400[c]
		4.0200[d]
$_{37}$Rb	[Kr]$5s^{1}_{+}$	3.9553
$_{38}$Sr	[Kr]$5s^{2}_{+}$	4.0730
$_{39}$Y	[Kr]$4d^{1}_{-}\,5s^{2}_{+}$	4.1979
$_{40}$Zr	[Kr]$4d^{2}_{-}\,5s^{2}_{+}$	4.3251
$_{41}$Nb	[Kr]$4d^{4}_{-}\,5s^{1}_{+}$	4.4823
$_{42}$Mo	[Kr]$4d^{4}_{-}\,5s^{2}_{+}$	4.6202
$_{43}$Tc	[Kr]$4d^{4}_{-}\,4d^{2}_{+}\,5s^{1}_{+}$	4.7587
$_{44}$Ru	[Kr]$4d^{4}_{-}\,4d^{3}_{+}\,5s^{1}_{+}$	4.8974
$_{45}$Rh	[Kr]$4d^{4}_{-}\,4d^{4}_{+}\,5s^{1}_{+}$	5.0597
$_{46}$Pd	[Kr]$4d^{4}_{-}\,4d^{6}_{+}$	5.2485
$_{47}$Ag	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{1}_{+}$	5.3771
$_{48}$Cd	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}$	5.5171
$_{49}$In	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{1}_{-}$	5.6396
$_{50}$Sn	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{2}_{-}$	5.7731
$_{51}$Sb	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{2}_{-}\,5p^{1}_{+}$	5.9022
$_{52}$Te	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{2}_{-}\,5p^{2}_{+}$	6.0297
$_{53}$I	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{2}_{-}\,5p^{3}_{+}$	6.1738
$_{54}$Xe	[Kr]$4d^{4}_{-}\,4d^{6}_{+}\,5s^{2}_{+}\,5p^{2}_{-}\,5p^{4}_{+}$	6.3152
		6.1400[c]
		6.6200[d]
$_{55}$Cs	[Xe]$6s^{1}_{+}$	6.4171
$_{56}$Ba	[Xe]$6s^{2}_{+}$	6.5375
$_{57}$La	[Xe]$5d^{1}_{-}\,6s^{2}_{+}$	6.6651
$_{58}$Ce	[Xe]$4f^{2}_{-}\,6s^{2}_{+}$	6.8458
$_{59}$Pr	[Xe]$4f^{3}_{-}\,6s^{2}_{+}$	7.0145
$_{60}$Nd	[Xe]$4f^{4}_{-}\,6s^{2}_{+}$	7.1674
$_{61}$Pm	[Xe]$4f^{5}_{-}\,6s^{2}_{+}$	7.3332
$_{62}$Sm	[Xe]$4f^{6}_{-}\,6s^{2}_{+}$	7.4984
$_{63}$Eu	[Xe]$4f^{6}_{-}\,4f^{1}_{+}\,6s^{2}_{+}$	7.6629
$_{64}$Gd	[Xe]$4f^{6}_{-}\,4f^{2}_{+}\,6s^{2}_{+}$	7.8015
$_{65}$Tb	[Xe]$4f^{6}_{-}\,4f^{3}_{+}\,6s^{2}_{+}$	7.9904
$_{66}$Dy	[Xe]$4f^{6}_{-}\,4f^{4}_{+}\,6s^{2}_{+}$	8.1535
$_{67}$Ho	[Xe]$4f^{6}_{-}\,4f^{5}_{+}\,6s^{2}_{+}$	8.3280
$_{68}$Er	[Xe]$4f^{6}_{-}\,4f^{6}_{+}\,6s^{2}_{+}$	8.5016
$_{69}$Tm	[Xe]$4f^{6}_{-}\,4f^{7}_{+}\,6s^{2}_{+}$	8.6743
$_{70}$Yb	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,6s^{2}_{+}$	8.8462
$_{71}$Lu	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{1}_{-}\,6s^{2}_{+}$	8.9891
$_{72}$Hf	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{2}_{-}\,6s^{2}_{+}$	9.1323
$_{73}$Ta	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{3}_{-}\,6s^{2}_{+}$	9.2894
$_{74}$W	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,6s^{2}_{+}$	9.4443
$_{75}$Re	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{1}_{+}\,6s^{2}_{+}$	9.5969
$_{76}$Os	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{2}_{+}\,6s^{2}_{+}$	9.7484
$_{77}$Ir	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{5}_{+}$	9.9385
$_{78}$Pt	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{5}_{+}\,6s^{1}_{+}$	10.0655
$_{79}$Au	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{1}_{+}$	10.2439
$_{80}$Hg	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}$	10.3928
$_{81}$Tl	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{1}_{-}$	10.5257
$_{82}$Pb	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{2}_{-}$	10.6674
$_{83}$Bi	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{2}_{-}\,6p^{1}_{+}$	10.8012
$_{84}$Po	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{2}_{-}\,6p^{2}_{+}$	10.9335
$_{85}$At	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{2}_{-}\,6p^{3}_{+}$	11.0821
$_{86}$Rn	[Xe]$4f^{6}_{-}\,4f^{8}_{+}\,5d^{4}_{-}\,5d^{6}_{+}\,6s^{2}_{+}\,6p^{2}_{-}\,6p^{4}_{+}$	11.2275
$_{87}$Fr	[Rn]$7s^{1}_{+}$	11.3378
$_{88}$Ra	[Rn]$7s^{2}_{+}$	11.4638
$_{89}$Ac	[Rn]$6d^{1}_{-}\,7s^{2}_{+}$	11.5939
$_{90}$Th	[Rn]$6d^{2}_{-}\,7s^{2}_{+}$	11.6284
$_{91}$Pa	[Rn]$5f^{2}_{-}\,6d^{1}_{-}\,7s^{2}_{+}$	11.8993
$_{92}$U	[Rn]$5f^{3}_{-}\,6d^{1}_{-}\,7s^{2}_{+}$	12.0540
$_{93}$Np	[Rn]$5f^{4}_{-}\,6d^{1}_{-}\,7s^{2}_{+}$	12.2228
$_{94}$Pu	[Rn]$5f^{6}_{-}\,7s^{2}_{+}$	12.4148
$_{95}$Am	[Rn]$5f^{6}_{-}\,5f^{1}_{+}\,7s^{2}_{+}$	12.5797
$_{96}$Cm	[Rn]$5f^{6}_{-}\,5f^{1}_{+}\,6d^{1}_{-}\,7s^{2}_{+}$	12.7230

TABLE II. (*Continued.*)

Atom	Relativistic electronic configuration[a]	$-E_{\mathrm{RC\Xi}}^{\mathrm{corr}}$ [b]	Atom	Relativistic electronic configuration[a]	$-E_{\mathrm{RC\Xi}}^{\mathrm{corr}}$ [b]
$_{97}$Bk	$[\mathrm{Rn}]5f_-^6\,5f_+^3\,7s_+^2$	12.9092	$_{102}$No	$[\mathrm{Rn}]5f_-^6\,5f_+^8\,7s_+^2$	13.4778
$_{98}$Cf	$[\mathrm{Rn}]5f_-^6\,5f_+^4\,7s_+^2$	13.0737	$_{103}$Lw	$[\mathrm{Rn}]5f_-^6\,5f_+^8\,6d_-^1\,7s_+^2$	13.6101
$_{99}$Es	$[\mathrm{Rn}]5f_-^6\,5f_+^5\,7s_+^2$	13.2497	104	$[\mathrm{Rn}]5f_-^6\,5f_+^8\,6d_-^2\,7s_+^2$	13.8743
$_{100}$Fm	$[\mathrm{Rn}]5f_-^6\,5f_+^6\,7s_+^2$	13.2801	105	$[\mathrm{Rn}]5f_-^6\,5f_+^8\,6d_-^3\,7s_+^2$	14.0305
$_{101}$Md	$[\mathrm{Rn}]5f_-^6\,5f_+^7\,7s_+^2$	13.3041	106	$[\mathrm{Rn}]5f_-^6\,5f_+^8\,6d_-^4\,7s_+^2$	14.2008

[a] The symbol + means $j = l + \frac{1}{2}$ and the symbol − means $j = l - \frac{1}{2}$.

[b] The exact correlation energy using Eq. (52) of text is given below the present value wherever available.

[c] Values by the gradient correction method of Langreth (GCL), quoted in Ref. 37.

[d] Values by the gradient correction method of Perdew (GCP) taken from Ref. 37.

which is calculated using Eq. (52), and with the values calculated by other methods. Presently, correlation energy is calculated by using Eq. (21). The deviation of correlation energy by the present RCΞ method from the exact correlation energy for first- and second-row atoms is given in Fig. 4. The error in correlation energy by the Voska, Wilk, and Nusair (VWN) method[30] and by the method of gradient correction due to Perdew[37,38] (GCP) is also given in Fig. 4. It is seen that the correlation energy calculated by Voska, Wilk, and Nusair is nearly about two times higher than the exact energy. The present method gives comparable correlation energies for first-row elements (with an average of 80% recovery), with the deviation being about 0.1 Ry. For the second-row elements, the RCΞ method gives better values with an average of 90% recovery of correlation energy. It is evident from the Fig. 4 that the present RCΞ method gives a reasonable correlation energy for atoms. Since correlation energy is not generally available in the literature for atoms with $Z > 18$, we have calculated it for the first time for all the atoms in the Periodic Table. These values are given in Table II along with the relativistic electron configuration. The available exact correlation energies are also given in Table II. The variation of correlation energy with atomic number is displayed in Fig. 5, which shows a near linear relationship for the entire range of the Periodic Table.

C. Spin-orbit parameter

In Table III, spin-orbit parameter values for various orbitals of the uranium atom calculated using the present

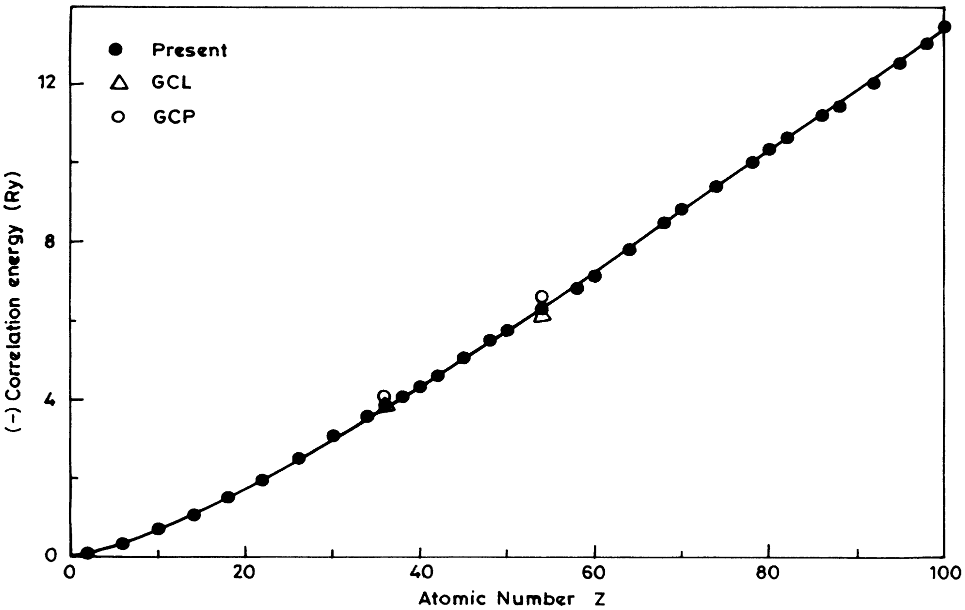

FIG. 5. Variation of correlation energy (Ry) vs atomic number ($2 \le Z \le 100$) by the present RCΞ method. Available values for atoms Kr and Xe by GCL (gradient correction due to Langreth, Ref. 37) and GCP (gradient correction due to Perdew, Ref. 37) are also indicated.

TABLE III. Spin-orbit parameter (Ry) for uranium.

Orbital	RΞ[a]	HFR[b]	DHF[c]	RCΞ[d]	Expt.[e]
$2p$	192.670	199.100	187.800	187.708	185.300
$3p$	43.989	46.200	43.72	43.178	43.000
$3d$	5.364	5.330	5.290	5.261	5.170
$4p$	11.355	11.980	11.540	11.299	11.200
$4d$	1.253	1.264	1.288	1.247	1.230
$4f$	0.227	0.221	0.250	0.234	0.230
$5p$	2.687	2.701	2.763	2.726	3.200
$5d$	0.239	0.230	0.334	0.246	0.260
$5f$	0.017	0.017			0.016
$6p$	0.431	0.427	0.539	0.477	0.490
$6d$	0.014	0.014			0.019

[a] Tabulated values taken from Ref. 4.
[b] Taken from Ref. 17.
[c] Dirac-Hartree-Fock values calculated using Eq. (56) of text.
[d] Present work calculated using Eq. (56) of text.
[e] Experimental values quoted in Ref. 17.

RCΞ method are compared with values obtained by the DHF method,[7] RΞ method,[4] and relativistic Hartree-Fock (HFR) method,[17] and with experimental results.[17] The spin-orbit parameter in the earlier RΞ method was calculated by perturbation as the RΞ method did not distinguish the spin-orbit levels with $l \neq 0$. The spin-orbit parameter values of the present method and the DHF method are calculated using the equation

$$\xi_{nl}=\frac{2}{(2l+1)}(\varepsilon_{nlj+}-\varepsilon_{nlj-}) , \tag{56}$$

TABLE IV. Expectation values of r^n ($n=-1$, 1, and 2) for uranium. RCΞ denotes values from the present work and DHF, the Dirac-Hartree-Fock values from Ref. 7.

	$\langle r^{-1}\rangle$		$\langle r\rangle$		$\langle r^2\rangle$	
Orbital[a]	RCΞ	DHF	RCΞ	DHF	RCΞ	DHF
$1s_+$	122.6458	122.4204	0.0136	0.0137	0.0003	0.0003
$2s_+$	28.9472	30.9612	0.0572	0.0565	0.0039	0.0039
$2p_-$	28.8703	30.8789	0.0466	0.0485	0.0027	0.0027
$2p_+$	22.8740	22.7759	0.0558	0.0560	0.0038	0.0038
$3s_+$	10.6670	11.2786	0.1477	0.1471	0.0249	0.0249
$3p_-$	10.5765	11.1748	0.1389	0.1383	0.0225	0.0224
$3p_+$	8.9604	9.0417	0.1567	0.1565	0.0285	0.0285
$3d_-$	8.8793	8.9245	0.1351	0.1352	0.0214	0.0215
$3d_+$	8.5320	8.4928	0.1398	0.1406	0.0228	0.0231
$4s_+$	4.6533	4.8202	0.3203	0.3198	0.1157	0.1156
$4p_-$	4.5477	4.7091	0.3190	0.3184	0.1158	0.1155
$4p_+$	3.9506	4.0003	0.3550	0.3534	0.1429	0.1419
$4d_-$	3.7787	3.8136	0.3517	0.3506	0.1424	0.1416
$4d_+$	3.6481	3.6629	0.3622	0.3613	0.1508	0.1502
$4f_-$	3.3903	3.3829	0.3504	0.3514	0.1435	0.1445
$4f_+$	3.3408	3.3265	0.3553	0.3567	0.1475	0.1487
$5s_+$	2.0997	2.1106	0.6672	0.6719	0.4975	0.5043
$5p_-$	1.9905	2.0009	0.6953	0.6996	0.5428	0.5492
$5p_+$	1.7515	1.7451	0.7739	0.7747	0.6717	0.6729
$5d_-$	1.5304	1.5223	0.8757	0.8701	0.8508	0.8597
$5d_+$	1.4778	1.4655	0.8957	0.8979	0.9108	0.9152
$5f_-$	0.9324	0.9359	1.4344	1.4227	2.5301	2.4954
$6s_+$	0.8952	0.8848	1.4746	1.4969	2.4297	2.5045
$6p_-$	0.7905	0.7898	1.6554	1.6636	3.0824	3.1137
$6p_+$	0.6810	0.6779	1.8976	1.8976	4.0615	4.0615
$6d_-$	0.4181	0.4104	3.0989	3.1519	11.3649	11.8269
$7s_+$	0.3164	0.2879	4.0004	4.4314	18.1521	21.4077

[a] Note that + means $j=l+\frac{1}{2}$ and − means $j=l-\frac{1}{2}$.

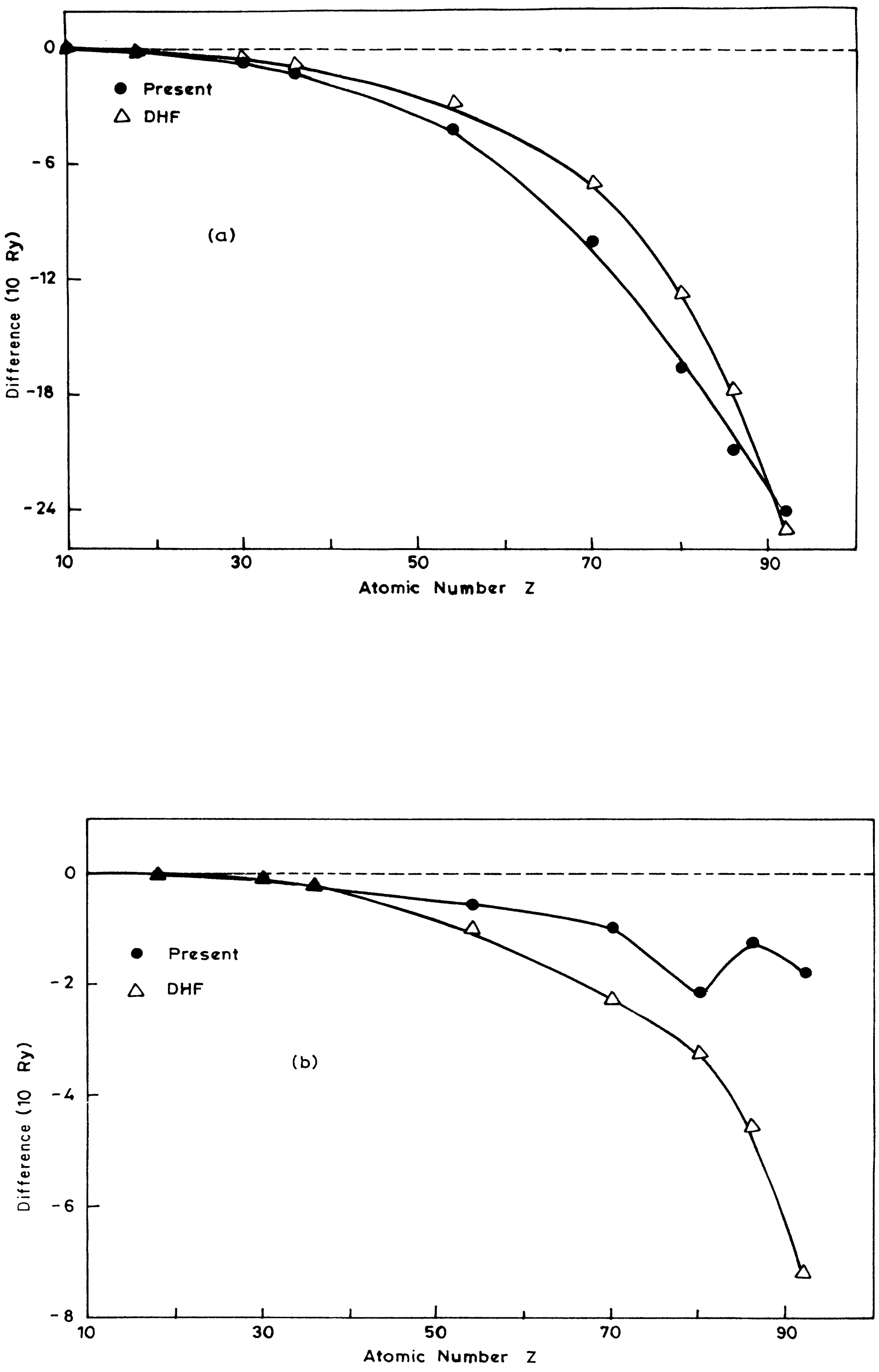

FIG. 6. Deviation of the spin-orbit parameter values from the experimental values by the RCΞ (this work) and DHF methods [calculated using Eq. (56) of text], vs atomic number for (a) $2p$ orbitals, (b) $3p$ orbitals, and (c) $3d$ orbitals.

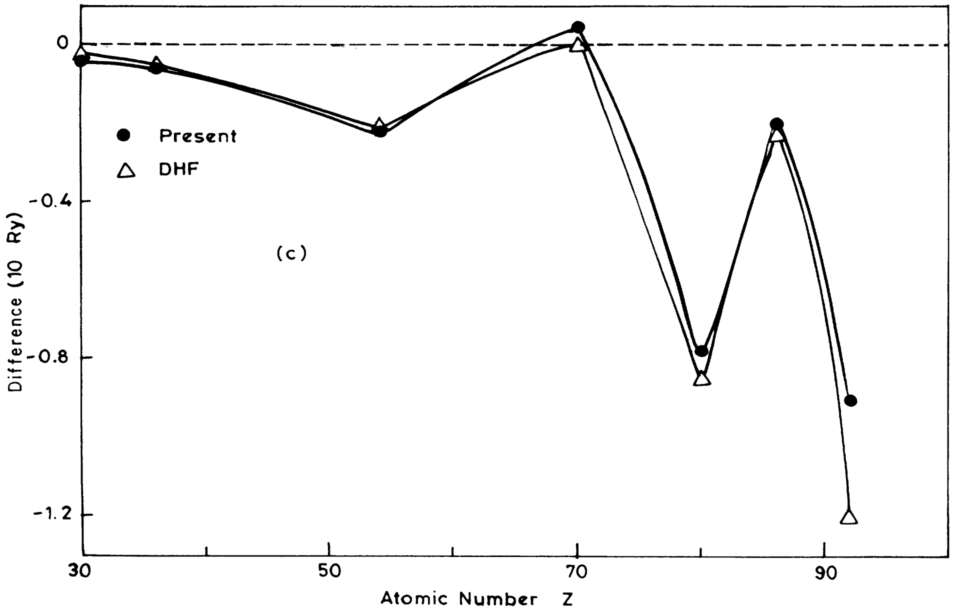

FIG. 6. (*Continued*).

where the ε's are the central-field eigenvalues in the respective methods. All the values for various orbitals calculated by the present method are better than that given by the RΞ method and HFR method, and are comparable to DHF results and experimental values (see Table III). This shows that spin-orbit interaction is treated well in the present method. The deviation of the spin-orbit parameter for orbitals 2*p*, 3*p*, and 3*d* in various atoms by the present method and the DHF method, from the experimental value, are given in Figs. 4(a)–4(c), respectively. For 2*p* and 3*d* orbitals, the deviation by the present method is almost the same as that by the DHF method. For the 3*p* orbital, the values by the present method are closer to experimental results. It is evident from the Table III and the figures, that the spin-orbit interaction is well described by the present RCΞ method.

D. Expectation values of r^n ($n = -1, 1, 2$)

The expectation values of r^{-1}, r, and r^2 for various orbitals of the uranium atom calculated by the present method are given in Table IV. The DHF results[7] are also given for comparison. The expectation values by the present method are seen to be in good agreement with the DHF values.

E. Ionization energy

Using the ΔSCF procedure, the ionization energies for the orbitals of some atoms, namely, Ar, Xe, and Hg are computed by the present method and are given in Table V. $\Delta E_{\mathrm{DFHS}}^{\mathrm{Breit}}$ represents the Breit interaction energy correction to the ionization energy and is calculated as the difference between the total Breit interaction energy of the atom and ion using the DHFS method.[54] The Breit energy values of Huang *et al.*[54] are assumed for the present method. The contribution of the correlation energy to ionization energy, $\Delta E_{\mathrm{RC}\Xi}^{\mathrm{corr}}$, given in column 1 of Table V is calculated as the difference between the correlation energy of the atom and its ion. The ionization energies by the present method are in good agreement with the experimental[53,54] as well as with the DHFS (ΔSCF) results. The close parallelism between the RCΞ method (single-component) and the DHFS (two-component) results indicates that a single-component wave function is of sufficient accuracy for calculating the ionization energy of atoms. It is seen that the contribution of correlation energy to the ionization energy is comparatively more than the Breit-interaction energy correction for the valence shell (*n* shell) and the $n-1$ shell. For the core orbital ionization energy, the contribution of the correlation energy is comparatively smaller than the Breit-interaction correction and is almost a constant for atoms given in Table V. To study the importance of correlation energy for the valence orbital ionization energy (VOIE), we have given the VOIE's for the first- and second-row elements in Table VI. The values in column 2 are computed by the Ξ (ΔSCF) method[1] (without correlation). The values by the present RCΞ (ΔSCF) method, which includes Coulomb correlation are closer to the experimental[55] results than that calculated by the Ξ and DHFS methods, which do not include such a correlation. This shows the importance of correlation to the VOIE's. This is true for the heavy atoms also. In Fig. 7, the deviation of the VOIE's by the present and DHFS methods from the experimental results is shown. For the present method, the deviation is comparatively smaller than that for the DHFS method (see Fig. 7). We conclude that correlation is important for valence orbital ionization and is less important for core orbital ionization.

It is known[56] that the negative of the Hartree-Fock eigenvalues agrees well with the experimental ionization energies for the valence-shell ionizations within the Koopmans approximation. This has been attributed[56] to an error compensation between orbital relaxation and correlation effects, which were supposed to be of similar magnitude but opposite in sign. Even though the Koopmans approximation is strictly not valid for local-density methods, we can study the relative importance of the

TABLE V. Orbital ionization energies (Ry) for Ar, Xe, and Hg.

Atom	Orbital[a]	$\Delta E^{\text{corr}}_{\text{RC}\Xi}$ [b]	$\Delta E^{\text{Breit}}_{\text{DHFS}}$ [c]	$I^{\Delta\text{SCF}}_{\text{RC}\Xi}$ [d]	$I^{\Delta\text{SCF}}_{\text{DHFS}}$ [e]	$I^{\text{expt.}}$ [e]
Ar	$1s_+$	0.1039	0.2460	235.6605	235.5898	235.6420
	$2s_+$	0.0905	0.0136	24.0718	24.0080	23.9840
	$2p_-$	0.0912	0.0140	18.4530	18.3700	18.4160
	$2p_+$	0.0912	0.0079	18.2828	18.2120	18.2620
	$3s_+$	0.0747		2.4755	2.4400	2.1540
	$3p_-$	0.0714		1.7443	1.0860	1.1710
	$3p_+$	0.0713		1.1587	1.0720	1.1580
Xe	$1s_+$	0.0952	9.1272	2540.2940	2540.2800	2540.3200
	$2s_+$	0.0897	0.9536	401.3314	401.2000	400.8200
	$2p_-$	0.0841	0.9776	375.9375	375.3400	375.4000
	$2p_+$	0.0835	0.6618	352.1791	351.8000	351.8800
	$3s_+$	0.0815	0.0674	84.9411	84.7000	84.4400
	$3p_-$	0.0820	0.1466	73.9544	73.8800	73.6600
	$3p_+$	0.0814	0.0888	69.5656	69.3200	69.1400
	$3d_-$	0.0820	0.0468	50.8742	50.6200	50.6400
	$3d_+$	0.0820	0.0126	49.9183	49.7000	49.7200
	$4s_+$	0.0743	0.0078	16.6295	16.1660	15.6700
	$4p_-$	0.0737	0.0226	12.6681	12.4140	10.6940
	$4p_+$	0.0732	0.0110	11.7872	11.5040	
	$4d_-$	0.0718		5.1812	5.0180	5.1080
	$4d_+$	0.0712		5.0121	4.8740	4.9620
	$5s_+$	0.0681		1.8751	1.9500	1.7120
	$5p_-$	0.0644	0.0016	1.0023	0.9260	0.9840
	$5p_+$	0.0640		0.8730	0.8280	0.8920
Hg	$1s_+$	0.0909	33.6666	6112.7229	6107.7600	6108.3800
	$2s_+$	0.0880	4.2088	1092.9593	1092.0000	1091.0200
	$2p_-$	0.0882	4.3540	1047.7023	1044.7000	1044.6800
	$2p_+$	0.0880	2.6566	904.1520	903.2800	903.2000
	$3s_+$	0.0874	0.3554	264.4569	263.4000	262.1200
	$3p_-$	0.0875	0.7759	242.4969	241.9400	241.3000
	$3p_+$	0.0873	0.4708	210.4565	210.2200	209.6000
	$3d_-$	0.0873	0.3492	178.2593	175.8800	175.6200
	$3d_+$	0.0873	0.2276	169.2885	169.2200	169.0000
	$4s_+$	0.0869	0.0653	60.2885	60.1000	59.1600
	$4p_-$	0.0868	0.1619	52.9224	50.9600	50.0800
	$4p_+$	0.0864	0.0853	44.6043	43.2400	42.3000
	$4d_-$	0.0861	0.0456	30.0364	28.5200	28.1400
	$4d_+$	0.0859	0.0195	28.4087	27.0800	26.7800
	$4f_-$	0.0842	−0.0102	8.3412	7.9840	7.8600
	$4f_+$	0.0841	−0.0208	7.9514	7.6860	7.5800
	$5s_+$	0.0788	0.0082	9.7887	9.8200	9.1800
	$5p_-$	0.0779	0.0239	6.6412	6.7200	6.2400
	$5p_+$	0.0768	0.0099	5.5234	5.3700	4.5600
	$5d_-$	0.0718	0.0011	1.2003	1.1042	1.2280
	$5d_+$	0.0710	−0.0014	1.0597	0.9752	1.0900
	$6s_+$	0.0547	0.0006	0.7375	0.6316	0.7680

[a] Note that the symbol + means $j=l+\frac{1}{2}$ and the symbol − means $j=l-\frac{1}{2}$.

[b] Contribution of correlation energy to the ionization energy.

[c] Correction of Breit interaction energy to the ionization energy taken from Ref. 54.

[d] Present work (with Breit-interaction correction).

[e] Taken from Ref. 54.

TABLE VI. Valence orbital ionization energy (Ry).

Atom	$I_{\Xi}^{\Delta SCF}$ [a]	$I_{RC\Xi}^{\Delta SCF}$ [b]	$I_{DHFS}^{\Delta SCF}$ [c]	Expt.[d]
Li	0.3928	0.4011	0.3916	0.3962
Be	0.5894	0.6737	0.5869	0.6851
B	0.5778	0.6217	0.5857	0.6098
C	0.7172	0.7641	0.6968	0.8279
N	0.8705	0.9288	0.9274	1.0687
O	1.0686	1.0947	1.0812	1.0011
F	1.2552	1.3322	1.2434	1.2809
Ne	1.4436	1.5188	1.4262	1.5847
Na	0.3616	0.3841	0.3569	0.3777
Mg	0.4855	0.5601	0.4828	0.5619
Al	0.4128	0.4468	0.4051	0.4398
Si	0.5214	0.5757	0.4987	0.5991
P	0.6453	0.6994	0.6642	0.8085
S	0.7803	0.8301	0.7794	0.7613
Cl	0.7272	1.0057	0.9296	0.9563
Ar	1.0798	1.1587	1.0721	1.1581

[a] Calculated using the ΔSCF procedure by the Ξ method (without correlation; see Ref. 1).

[b] Present work (with correlation).

[c] Taken from Ref. 54.

[d] Experimental values taken from Ref. 55.

three effects, namely, relaxation, correlation, and relativistic effects on the ionization energy of valence and core shells in the RCΞ formalism.

The contributions of relativistic effects ΔI^{rel} of Coulomb correlation ΔI^{corr} and of orbital relaxations ΔI^{relax} to the ionization of Ne and Kr atoms are calculated using Eqs. (57)–(59), respectively:

$$\Delta I_{RC\Xi}^{rel} = I_{RC\Xi}^{\Delta SCF} - I_{\Xi}^{\Delta SCF} - \Delta I_{RC\Xi}^{corr} \ , \tag{57}$$

$$\Delta I_{RC\Xi}^{corr} = E_{RC\Xi}^{corr}(X^{+}) - E_{RC\Xi}^{corr}(X) \ , \tag{58}$$

$$\Delta I_{RC\Xi}^{relax} = I_{\Xi}^{\Delta SCF} - [\varepsilon_i(\mathrm{HF})]_{\Xi} \ , \tag{59}$$

where $I_{RC\Xi}^{\Delta SCF}$ and $I_{\Xi}^{\Delta SCF}$ are ionization energy calculated by the RCΞ and Ξ methods, respectively; $E_{RC\Xi}^{corr}(X)$ and $E_{RC\Xi}^{corr}(X^{+})$ are correlation energies of the atom and its ion calculated by present method; and $\varepsilon_i(\mathrm{HF})_{\Xi}$ is the eigenvalue of the ith orbital calculated using the Ξ wave function in the Hartree-Fock expression[18] for the orbital eigenvalue. It is assumed that the $\Delta I_{RC\Xi}^{relax}$ is the same for the RCΞ and Ξ methods. In Fig. 8, the three contributions to the ionization potential, given by Eqs. (57)–(59) are plotted for Ne and Kr.

It is seen that the relativistic effect is dominant for the core shell ionization compared to correlation and relaxation effects for Kr, but it is less important for the lighter atom, Ne. Relaxation energy is greater than correlation energy for core shell ionization of Ne and Kr atoms. So they do not cancel each other for core shell ionization. It is evident from the Fig. 8 that there is no exact cancellation between relaxation and correlation energies, even for valence shell ionization of Ne and Kr. It is also interesting to note that the relativistic effect is as important as the other effects, even for valence shell ionization of the Kr atom.

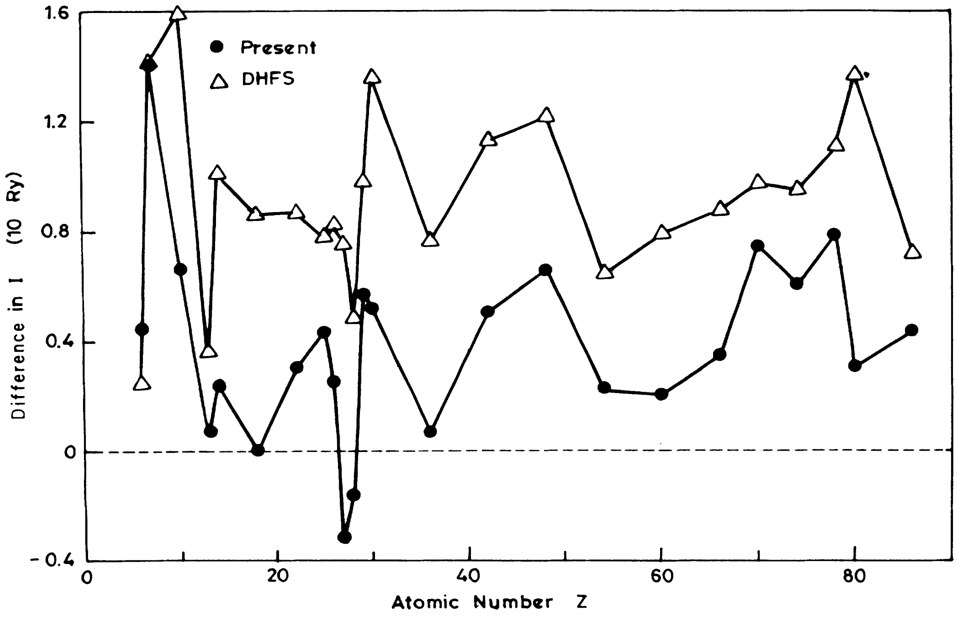

FIG. 7. Deviation of the valence orbital ionization energies (Ry) from experimental results by the RCΞ (this work) and DHFS (Ref. 54) methods, vs atomic number.

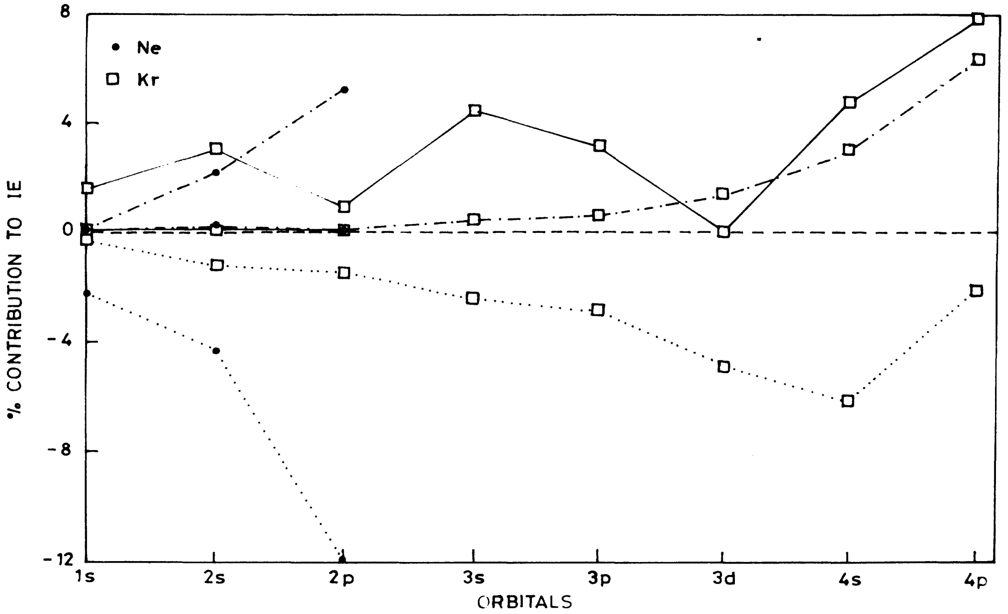

FIG. 8. Comparison of percentage of relativistic, correlation, and relaxation effects on ionization energy. (——) denotes the percentage of relativistic effect, —·—·— represents the percentage of correlation effect, and · · · · denotes the percentage of relaxation effect on ionization energy. Results for Ne and Kr are shown.

F. Electron affinity

The electron affinity of an atom is the difference between the total energies of the ground states of the atom and its negative ion. The quantity is positive for a stable negative ion and is zero or negative for unstable ions. Since the electron affinity is of the order of a few eV it is necessary to know the total energies of the atom and its negative ion accurately. Therefore it is essential to include correlation explicitly in calculating total energies. The electron affinity of various atoms has been calculated by many theories such as configuration interaction,[57] solving two- and three-particle Bethe-Goldstone equations,[58] electron-pair theories,[59] and local-density methods.[29,60]

Presently, the electron affinity of various atoms has been calculated using the RCΞ method and the Ξ method[1] (without correlation). Electron affinities thus obtained with correlation and without correlation are shown in Table VII and compared with the experimental values.[61] The percentage change due to correlation is given in parentheses. The negative ions of Li, B, C, and Na are predicted to be unstable by the Ξ method, but the RCΞ method correctly predicts them to be stable. We thus find that correlation is very important for predicting the stability of the negative ions. Further, electron affinity values are dramatically improved to the order of several hundred percent by the inclusion of the Coulomb correlation.

VI. CONCLUSIONS

In this paper, we have developed a fully correlated relativistic local-density method, called the RCΞ method, for atoms. All the major relativistic corrections and the two types of correlations, namely, the Fermi and Coulomb correlations, are explicitly incorporated in the formalism. The method is exactly self-interaction corrected. The Coulomb correlation is treated separately

TABLE VII. Electron affinity (eV), calculated using the Ξ method (Ξ, Ref. 1) and present method (RCΞ); the percentage change due to correlation and experimental values from Ref. 61 are also given.

Atom	Ξ	RCΞ	Change due to correlation (%)	Expt.
Li	−0.126	0.451	458	0.621
B	−0.837	0.361	143	0.281
C	−0.705	0.781	211	1.251
O	0.645	1.584	145	1.461
F	1.299	2.438	287	3.416
Na	−0.082	0.331	506	0.546
Si	0.214	0.819	282	1.404
S	1.683	2.709	60	2.081
Cl	2.809	3.291	17	3.651
Br	0.133	2.987	2154	3.364
I	3.401	3.781	11	3.061

and the form of the Coulomb-hole potential is derived from the cusp condition on the wave function, which is important for the proper description of short-range correlation. The present method has only a single universal parameter for all atoms, which represents the ratio of the Coulomb- and Fermi-hole radii. Computationally, the method is extremely simple and fast, and it has been implemented on a desktop PC.

The correlation energies calculated by the present method are in good agreement with available exact values. We have presented the correlation energy for all the atoms in the Periodic Table. The results for quantities such as total energy, expectation values of r^n ($n=1,-1,2$), and spin-orbit parameters are shown to be of near DHF accuracy. The effect of relativistic corrections and correlation on atomic properties such as ionization energy and electron affinity is discussed. The single-component RCΞ wave functions are shown to be accurate enough for ionization energy calculations. Coulomb correlation is of extreme importance in predicting the stability of negative ions and in obtaining reliable values of electron affinity.

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